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# PATENT ABSTRACTS OF JAPAN

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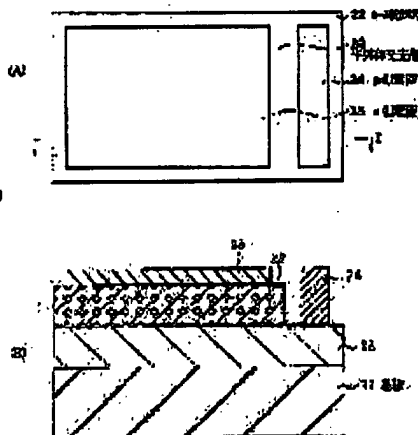
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## (54) LIGHT EMITTING ELEMENT AND MANUFACTURING METHOD THEREFOR

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a light emitting element which can easily be manufactured and operated, and to provide a manufacturing method.

**SOLUTION:** A structure where a hole transportation layer 22 and a semiconductor light emitting layer 23 are sequentially laminated on a substrate 21 is provided. The hole transportation layer 22 is constituted of the nitride of a 3B group element to which acceptor impurity is added. The semiconductor light emitting layer 23 is constituted of a fine grain sintered body. In the fine grain sintered body, fine grains including crystallite constituted of the oxide of ZnO are joined by sintering, a grain boundary energy barrier among the fine grains is small and electron transportation property is given. Thus, it can easily be operated by the DC current of low voltage. The substrate 21 can arbitrarily be selected, an area is made to be large and cost can be reduced. Then, the minute control of the hole transportation layer, the crystal system of the semiconductor light emitting layer 23 and a lattice constant is not necessary and the element can easily be manufactured.



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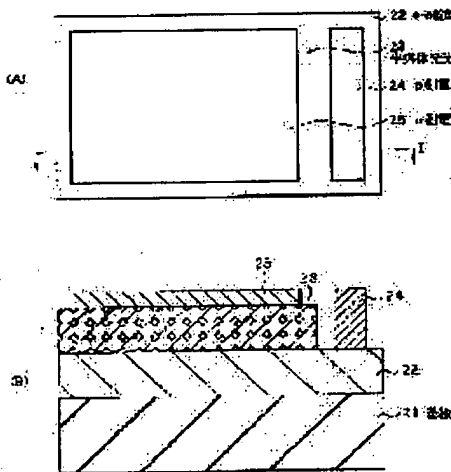
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**SOLUTION:** A structure where a hole transportation layer 22 and a semiconductor light emitting layer 23 are sequentially laminated on a substrate 21 is provided. The hole transportation layer 22 is constituted of the nitride of a 3B group element, to which acceptor impurity is added. The semiconductor light emitting layer 23 is constituted of a fine grain sintered body. In the fine grain sintered body, fine grains including crystallite constituted of the oxide of ZnO are jointed by sintering, a grain boundary energy barrier among the fine grains is small and electron transportation property is given. Thus, it can easily be operated by the DC current of low voltage. The substrate 21 can arbitrarily be selected, an area is made to be



large and cost can be reduced. Then, the minute control of the hole transportation layer, the crystal system of the semiconductor light emitting layer 23 and a lattice constant is not necessary and the element can easily be

manufactured.

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## CLAIMS

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[Claim(s)]

[Claim 1] A light emitting device comprising:

A hole transporting bed.

A semiconductor light layer which particles which are formed in the whole surface side of this hole transporting bed, and contain micro crystallite of a semiconductor become from a particle sintered compact joined by sintering region.

The 1st electrode electrically connected to said hole transporting bed.

The 2nd electrode electrically connected to said semiconductor light layer.

[Claim 2] The light emitting device according to claim 1, wherein said semiconductor light layer has an electron transportation function.

[Claim 3] The light emitting device according to claim 1, wherein a crystal grain diameter of micro crystallite in said particle sintered compact is 100 nm or less.

[Claim 4] The light emitting device according to claim 1, wherein micro crystallite in said particle sintered compact is constituted with an oxide containing at least one sort in a group which consists of zinc (Zn), titanium (Ti), and iron (Fe), or a nitride of 3B group element.

[Claim 5] The light emitting device according to claim 1, wherein micro crystallite in said particle sintered compact is constituted with a zinc oxide (ZnO).

[Claim 6] The light emitting device according to claim 1, wherein said hole transporting bed has larger forbidden-band width energy than said semiconductor light layer.

[Claim 7] The light emitting device according to claim 1, wherein said hole transporting bed is constituted with a nitride of 3B group element containing acceptor impurity.

[Claim 8] The light emitting device according to claim 7, wherein a nitride of said 3B group element is at least one sort in a group which consists of boron nitride (BN), aluminum nitride (AlN), gallium nitride (GaN), and a gallium-aluminum-nitride mix crystal (AlGaN).

[Claim 9] The light emitting device according to claim 7, wherein said acceptor impurity is magnesium (Mg).

[Claim 10] The light emitting device according to claim 1, wherein said hole transporting bed is constituted with a single crystal body, the polycrystalline substance, amorphous bodies, particle objects, or these complexes.

[Claim 11] The light emitting device according to claim 1, wherein said 1st electrode and said 2nd electrode contain gold (Au) at least.

[Claim 12] The light emitting device according to claim 1, wherein said 1st electrode has the structure which laminated a nickel layer, a platinum layer, and a gold layer.

[Claim 13] The light emitting device according to claim 1, wherein said 1st electrode and said 2nd electrode are alloyed.

[Claim 14] A light emitting device comprising:

A hole transporting bed.

An electron transport layer.

A semiconductor light layer which particles which are formed between these hole transporting bed and an electron transport layer, and contain micro crystallite of a semiconductor become from a particle sintered compact joined by sintering region.

The 1st electrode electrically connected to said hole transporting bed, and the 2nd electrode electrically connected to said electron transport layer.

[Claim 15]The light emitting device according to claim 14, wherein a crystal grain diameter of micro crystallite in said particle sintered compact is 100 nm or less.

[Claim 16]The light emitting device according to claim 14, wherein micro crystallite in said particle sintered compact is constituted with an oxide containing at least one sort in a group which consists of zinc (Zn), titanium (Ti), and iron (Fe), or a nitride of 3B group element.

[Claim 17]The light emitting device according to claim 14, wherein micro crystallite in said particle sintered compact is constituted with a zinc oxide (ZnO).

[Claim 18]The light emitting device according to claim 14, wherein said hole transporting bed and said electron transport layer have larger forbidden-band width energy than said semiconductor light layer.

[Claim 19]The light emitting device according to claim 14, wherein said hole transporting bed is constituted with a nitride of 3B group element containing acceptor impurity.

[Claim 20]The light emitting device according to claim 19, wherein said acceptor impurity is magnesium (Mg).

[Claim 21]The light emitting device according to claim 14, wherein said electron transport layer is constituted with a nitride of 3B group element containing donor impurities.

[Claim 22]The light emitting device according to claim 21, wherein said donor impurities are silicon (Si).

[Claim 23]The light emitting device according to claim 14, wherein said hole transporting bed and said electron transport layer are constituted with a single crystal body, the polycrystalline substance, amorphous bodies, particle objects, or these complexes.

[Claim 24]A light emitting device comprising:

A semiconductor light layer which particles containing micro crystallite of a semiconductor become from a particle sintered compact joined by sintering region.

The 1st electrode and 2nd electrode that were electrically connected with this semiconductor light layer, respectively.

[Claim 25]A manufacturing method of a light emitting device characterized by comprising the following.

A process of forming a hole transporting bed on a substrate.

A process of forming a semiconductor light layer on this hole transporting bed with a particle sintered compact which sintered particles containing micro crystallite of a semiconductor.

[Claim 26]A manufacturing method of the light emitting device according to claim 25 forming with an oxide containing at least one sort in a group which consists said micro crystallite of zinc (Zn), titanium (Ti), and iron (Fe), or a nitride of 3B group element.

[Claim 27]A manufacturing method of the light emitting device according to claim 25 forming said micro crystallite with a zinc oxide (ZnO).

[Claim 28]A manufacturing method of the light emitting device according to claim 25 sintering said particle by irradiating with heat-treatment or an energy beam.

[Claim 29]A manufacturing method of the light emitting device according to claim 28 sintering said particle by irradiating with an excimer laser beam.

[Claim 30]A manufacturing method of the light emitting device according to claim 29 sintering said particle by irradiating with an excimer laser beam oscillated using XeCl, XeF, XeBr, KrF, KrCl, ArF, or F<sub>2</sub>.

[Claim 31]A manufacturing method of the light emitting device according to claim 25 sintering said particle in an oxygen containing atmosphere or nitrogen

content atmosphere.

[Claim 32]A manufacturing method of the light emitting device according to claim 25, wherein a content ratio of oxygen or nitrogen sinters said particle in a gas atmosphere beyond 60mol%.

[Claim 33]A manufacturing method of the light emitting device according to claim 25 making it dry and sintering after applying a coating solution which made a solution distribute said particle on said hole transporting bed.

[Claim 34]A manufacturing method of the light emitting device according to claim 33 using an organic solvent containing at least one sort of organic compounds which have one or more hydroxyl groups as said solution.

[Claim 35]A manufacturing method of the light emitting device according to claim 34, wherein said organic compound is chosen from alcohol and its derivative, phenol, and cresol.

[Claim 36]A manufacturing method of the light emitting device according to claim 33 applying said coating solution using a spin coat method, a dip coating method, a spray coating method, the roll coat method, the meniscus coat method, the bar coat method, the curtain flow coat method, or the bead coat method.

[Claim 37]A manufacturing method of a light emitting device characterized by comprising the following.

A process of forming a hole transporting bed on a substrate.

A process of forming a semiconductor light layer on this hole transporting bed with a particle sintered compact which sintered particles containing micro crystallite of a semiconductor.

A process of forming an electron transport layer on this semiconductor light layer.

[Claim 38]A manufacturing method of the light emitting device according to claim 37 forming with an oxide containing at least one sort in a group which consists said micro crystallite of zinc (Zn), titanium (Ti), and iron (Fe), or a nitride of 3B group element.

[Claim 39]A manufacturing method of the light emitting device according to claim 37 forming said micro crystallite with a zinc oxide (ZnO).

[Claim 40]A manufacturing method of the light emitting device according to claim 37 sintering said particle by irradiating with heat-treatment or an energy beam.

[Claim 41]A manufacturing method of the light emitting device according to claim 40 sintering said particle by irradiating with an excimer laser beam.

[Claim 42]A manufacturing method of the light emitting device according to claim 41 sintering said particle by irradiating with an excimer laser beam oscillated using XeCl, XeF, XeBr, KrF, KrCl, ArF, or F<sub>2</sub>.

[Claim 43]A manufacturing method of the light emitting device according to claim 37 sintering said particle in an oxygen containing atmosphere or nitrogen content atmosphere.

[Claim 44]A manufacturing method of the light emitting device according to claim 37, wherein a content ratio of oxygen or nitrogen sinters said particle in a gas atmosphere beyond 60mol%.

[Claim 45]A manufacturing method of the light emitting device according to claim 37 making it dry and sintering after applying a coating solution which made a solution distribute said particle on said hole transporting bed.

[Claim 46]A manufacturing method of the light emitting device according to claim 45 using an organic solvent containing at least one sort of organic compounds which have one or more hydroxyl groups as said solution.

[Claim 47]A manufacturing method of the light emitting device according to claim 46, wherein said organic compound is chosen from alcohol and its derivative, phenol, and cresol.

[Claim 48]A manufacturing method of the light emitting device according to claim 45 applying said coating solution using a spin coat method, a dip coating

method, a spray coating method, the roll coat method, the meniscus coat method, the bar coat method, the curtain flow coat method, or the bead coat method.

[Claim 49] A manufacturing method of a light emitting device including a process of forming a semiconductor light layer on a substrate with a particle sintered compact which sintered particles containing micro crystallite of a semiconductor.

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#### DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a light emitting device using the particle sintered compact containing the micro crystallite of a semiconductor, and a manufacturing method for the same.

[0002]

[Description of the Prior Art] Also in the light emitting device which operates according to a direct current, especially a blue light-emitting diode (Blue-LED; Blue Light Emitting Diode), as a practical semiconductor material used for light emitting devices, such as an ultraviolet light emitting diode (UV-LED; Ultra-Violet Light Emitting Diode), Gallium nitride (GaN), an indium nitride gallium mix crystal (InGaN), 3 fellows nitride compound semiconductor represented by a gallium-aluminum-nitride mix crystal (AlGaN) or the indium nitride aluminum gallium mix crystal (InAlGaN) attracts attention, and the research and development are done actively.

[0003] Such a 3 fellows nitride compound semiconductor, the former, MOCVD (Metal Organic Chemical.) Vapor Deposition; organometal chemistry vapor phase epitaxy -- law (it is also called the MOVPE (Metal Organic Vapor Phase Epitaxy) method) or MBE (Molecular Beam Epitaxy; molecular beam epitaxy) -- law. It is produced as a single crystal film by using and making it grow up on a substrate.

[0004] Among these, the MOCVD method is the method of carrying out heteroepitaxial growth of the 3 fellows nitride compound semiconductor on a substrate by carrying out the chemical reaction of the material gas of three group elements and nitrogen.

It has the advantage that a single crystal film with a uniform presentation can be formed.

Since substrate temperature (growing temperature) can be set up highly, it also has the advantage that a high, what is called crystalline single crystal film with few lattice defects, such as a rearrangement, can be produced comparatively easily.

[0005] On the other hand, an MBE technique is a method of irradiating a substrate with each particle beam of three group elements and nitrogen evaporated from the Knudsen cell, and growing up a crystal.

In order that forming a presentation and the uniform thin film of thickness might control desorption of nitrogen from a thin film surface at the time of growth in addition to a difficult thing, substrate temperature had to be made low, and there was a problem that it was difficult to produce a high crystalline single crystal film.

It is said that it generally depends for the luminous efficiency of a light emitting device to crystallinity strongly, therefore, under the present circumstances, the practically effective MOCVD method is used abundantly.

[0006] However, when manufacturing a light emitting device by the MOCVD method, the substrate to be used has a crystal lattice constant almost equal to the compound semiconductor to grow up, and it needs to be excellent in heat resistance. That is, the construction material and the size of a substrate had a problem that restrictions will arise.

[0007]For example, when growing up 3 fellows nitride compound semiconductor, the crystalline sapphire ( $\alpha$ -aluminum  $2O_3$ ) board is mainly used. This sapphire has 3 fellows nitride compound semiconductor and a crystal lattice constant especially almost equal to gallium nitride, and it is excellent in heat resistance.

It is a material suitable as a substrate for MOCVD.

However, to use silicon on sapphire, in order to make it grow up on c side, the processability and moldability of a substrate had difficulty and there was a problem to which material cost becomes high.

[0008]Since it was difficult to form the thin film of uniform thickness all over a substrate, a substrate with a big area could not be used, but under the present circumstances, it is about 20 cm at the maximum, and there was also a problem that productivity was low.

[0009]Since a light emitting device serves as multilayer structure which comprises a luminous layer (it is also called an active layer) and a carrier transport layer, it needs to grow a compound semiconductor epitaxially so that crystalline-lattice distortion may not arise in the plane of composition of each semiconductor layer. It is because crystal lattice defects, such as a rearrangement, will occur [ near the plane of composition of each semiconductor layer ] and luminous efficiency will fall as the reason, if crystalline-lattice distortion arises. That is, the crystal system and grating constant of each semiconductor layer needed to be controlled precisely, it reached to an extreme of difficulty for setting out and its control of crystal growth conditions, and there was also a problem that manufacture was difficult.

[0010]There is an oxide semiconductor as a practical semiconductor material used for a light emitting device other than the above-mentioned 3 fellows nitride compound semiconductor. The feature of an oxide semiconductor is being able to grow up a crystal at low temperature compared with 3 fellows nitride compound semiconductor.

[0011]Also in the oxide semiconductor, the zinc oxide (ZnO) is known as a transited [ directly ] type luminescent material whose forbidden-band width energy is 3.2 eV, for example. It is thought that the exciton binding energy of a zinc oxide is 60meV, and is large compared with 24meV of gallium nitride, and an exciton exists stably also at a room temperature. Therefore, a large number [ the light emitting device which carries out exciton emission in a room temperature can be realized, and / the literature about the exciton emission of a zinc oxide ] in the past.

[0012]For example, as oldest publicly known literature about the light emitting device using the zinc oxide as a luminous layer, there is "ZINC OXIDE LIGHT EMITTING DIODE" (U. S. Patent: No. 4081764, Date: March 28-1978). In this literature, an anode electrode and a cathode terminal are formed in the flake of a single crystal zinc oxide, and the light emitting device of MS (Metal Semiconductor) structure of impressing direct current voltage to inter-electrode [ that ], and operating it is proposed. Generally, the light emitting device of MS structure makes a rectifying characteristic reveal using Schottky barrier (Schottky barrier) formed in a semiconductor surface by contact of metal and a semiconductor, and is operated. The feature of the light emitting device proposed by this patent is at the point of making a rectifying characteristic revealing, by exposing the crystal plane of an oxygen atom on one side of the flake of a single crystal zinc oxide, and forming the anode electrode which used a large material of the work function for that crystal plane. Therefore, in this light emitting device, there was a problem that the process technology to which the process technology to which the crystal plane of a single crystal zinc oxide is exposed precisely, and this crystal plane and anode electrode are joined exactly was indispensable, and manufacture was difficult.

[0013]In the past literature, the light emitting device of the MIS (Metal Insulator Semiconductor) structure of operating according to direct-current pulse current (frequency; 10 Hz - 1 kHz) other than the light emitting device of the

above-mentioned MS structure is proposed. The light emitting device of this MIS structure is a general term for the light emitting device which impresses voltage to a metal electrode and controls a semiconductor surface via an insulating material.

[0014] For example, as such a light emitting device, The thing of the structure which laminated the electrode of a silver (Ag) electrode, the insulating layer which consists of silicon oxide (SiO<sub>2</sub>), the luminous layer which consists of a zinc oxide which added lithium (Li), and silver one by one (B. W. Thomas et al.: Electronics Letters, vol.9, No.16, p.362(1973)., the thing (T. Minami et al.: Jpn.J.Appl.Phys., vol.13, No.9, p.1475(1974).) of the structure which laminated the electrode of a golden (Au) electrode, the insulating layer which consists of silicon oxide, the luminous layer which consists of zinc oxides, and gold one by one -- further, There are a thing (A. Shimizu et al.: Jpn.J.Appl.Phys., vol.17, No.8, p.1435(1978).) etc. of a golden electrode, the insulating layer which consists of zinc oxides, the luminous layer which consists of zinc oxides, and the structure which laminated the electrode of indium (In) one by one. The feature of these MIS structure light emitting device is at the point of using not current control but voltage control, on the structure. Therefore, the light emitting device of MIS structure cannot be operated by a direct current of a cell etc., and is made to operate by direct-current pulse current, such as a pulse generator. Therefore, the drive circuit which generates direct-current pulse current was needed, and there was a problem that the price of the whole system will become high. On the principle, for the structure which introduces an insulating layer, there was also a problem of a dielectric breakdown that an over-current flowed at the time of a drive, and reliability and stability had a technical problem.

[0015] In the latest publicly known literature, the light emitting device which carries out laser oscillation using the luminous layer of the zinc oxide constituted from micro crystallite of hexagonal prism structure is proposed (JP,10-256673,A "OPTO semiconductor device and manufacturing method for the same"). The feature of this light emitting device is at the point of operating positively the grain boundary (six sides) of the zinc oxide which consists of micro crystallite of hexagonal prism structure as a resonator mirror. Therefore, in this light emitting device, the hexagonal prism structure of micro crystallite was made to form precisely geometrically, and there was a problem that the production technology of controllable micro crystallite was indispensable, and manufacture was difficult, about the side interval of this hexagonal prism.

[0016] In addition, in the latest publicly known literature. Micro crystallite with equal particle diameter with the mean particle diameter of 20 nm or less. The monolayer put in order regularly or the n-type semiconductor luminous layer of multilayer film composition. The used light emitting device is proposed ("ELECTROLUMINESCENT DEVICES FORMED USING SEMICONDUCTOR NANOCRYSTALS AS AN ELECTRON TRANSPORT.). MEDIA AND METHOD OF MAKING SUCH ELECTROLUMINESCENT DEVICES" (U. S. Patent: No.5537000, Date: July 16-1996). By using micro crystallite with equal particle diameter with the mean particle diameter of 20 nm or less, a quantum size effect is revealed and the feature of this light emitting device is that it can control a luminous wavelength with a crystal grain diameter. Therefore, by this light emitting device, the problem that the grain boundary between micro crystallite needs to exist clearly in order to make a quantum size effect reveal, therefore the surface energy between micro crystallite will become large inevitably, and driver voltage will become high can be considered.

[0017]

[Problem(s) to be Solved by the Invention] This invention was made in view of this problem, and the purpose can be manufactured easily and there is in providing a light emitting device which can be operated easily, and a manufacturing method for the same.

[0018]



[Means for Solving the Problem]A light emitting device of this invention is characterized by comprising:

Hole transporting bed.

A semiconductor light layer which particles which are formed in the whole surface side of this hole transporting bed, and contain micro crystallite of a semiconductor become from a particle sintered compact joined by sintering region.

The 1st electrode electrically connected to said hole transporting bed.

The 2nd electrode electrically connected to said semiconductor light layer.

[0019]Other light emitting devices of this invention are characterized by comprising:

Hole transporting bed.

Electron transport layer.

A semiconductor light layer which particles which are formed between these hole transporting bed and an electron transport layer, and contain micro crystallite of a semiconductor become from a particle sintered compact joined by sintering region.

The 1st electrode electrically connected to said hole transporting bed, and the 2nd electrode electrically connected to said electron transport layer.

[0020]Other light emitting devices of this invention are characterized by comprising:

A semiconductor light layer which particles containing micro crystallite of a semiconductor become from a particle sintered compact joined by sintering region.

The 1st electrode and 2nd electrode that were electrically connected with this semiconductor light layer, respectively.

[0021]A manufacturing method of a light emitting device by this invention includes a process of forming a hole transporting bed on a substrate, and a process of forming a semiconductor light layer on this hole transporting bed with a particle sintered compact which sintered particles containing micro crystallite of a semiconductor.

[0022]A process at which a manufacturing method of other light emitting devices by this invention forms a hole transporting bed on a substrate, A process of forming a semiconductor light layer on this hole transporting bed with a particle sintered compact which sintered particles containing micro crystallite of a semiconductor, and a process of forming an electron transport layer on this semiconductor light layer are included.

[0023]In a light emitting device and other light emitting devices by this invention, if current is injected into a semiconductor light layer via the 1st electrode and 2nd electrode, light will occur in a semiconductor light layer. Here, since a semiconductor light layer is constituted by particle sintered compact to which particles containing micro crystallite of a semiconductor were joined in a sintering region, carrier transport nature in a semiconductor light layer is secured.

[0024]In a manufacturing method of a light emitting device by this invention, and a manufacturing method of other light emitting devices, a semiconductor light layer is formed with a particle sintered compact which sintered particles containing micro crystallite of a semiconductor.

[0025]

[Embodiment of the Invention]Hereafter, an embodiment of the invention is described in detail with reference to drawings.

[0026]Drawing 1 expresses notionally the example of 1 composition of the particle sintered compact 10 which constitutes the semiconductor light layer of the light emitting device concerning an embodiment of the invention. Drawing 1 expresses that composition notionally, in order to explain this particle sintered

compact 10 to the last, and it is not what described thing.

[0027]This particle sintered compact 10 has the structure where the particles 11 containing the micro crystallite which consists of semiconductors were joined by the sintering region 11a. This is obtained by sintering the particles 11 as shown in drawing 2. As opposed to a high grain boundary energy barrier (double Schottky barrier) existing in the interface between particles in the aggregate of the particles 11 shown in drawing 2, and there being no carrier transport nature, in this particle sintered compact 10, the grain boundary energy barrier between particles becomes small by the sintering region 11a, and the carrier transport nature between particles can be secured now. Thereby, this particle sintered compact 10 can obtain now the carrier transport nature about 0.001ohm of specific resistance cm - 10000-ohmcm, for example.

[0028]The particles 11 which constitute this particle sintered compact 10 may contain the particles which at least the part is constituted by micro crystallite, for example, may contain other particles other than micro crystallite and micro crystallite and by which the enveloping layer etc. were provided in micro crystallite. Micro crystallite is particles which consist of a single crystal or polycrystal here. As for the crystal grain diameter (namely, crystal grain diameter of one single crystal) of this micro crystallite, it is preferred that it is 100 nm or less. It is because a crystal with very few defects can be obtained if it is 100 nm or less. The crystal grain diameter of more desirable micro crystallite is 50 nm or less. It is because the surface free energy of micro crystallite increases, refining on the surface of micro crystallite and solid phase sintering between micro crystallite become more possible by heat-treatment or laser annealing processing at a low temperature service as a crystal grain diameter becomes small, so light emitting luminance and a mechanical strength can be raised.

[0029]This particle sintered compact 10 carries out forbidden-band transition luminescence (luminescence resulting from forbidden-band transition), or a donor acceptor pair emission (luminescence resulting from transition between donor acceptor level). That is, this particle sintered compact 10 has a forbidden-band transition luminescence function or a donor acceptor pair emission function, respectively.

[0030]The oxide containing at least one sort in the group which an oxide or a nitride is mentioned, for example, for example, consists of zinc (Zn), titanium (Ti), and iron (Fe) as a semiconductor which constitutes micro crystallite, or the nitride of 3B group element is preferred. Specifically A zinc oxide, titanium oxide ( $\text{TiO}_2$ ), iron oxide ( $\text{Fe}_2\text{O}_3$  or  $\text{FeO}$ ), A zinc oxide and a titanium oxide ( $\text{ZnO-TiO}_2$ ) mix crystal, a zinc oxide and an iron oxide ( $\text{ZnO-Fe}_2\text{O}_3$ ) mix crystal, or titanium oxide, an iron oxide ( $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ ) mix crystal, etc., Or gallium nitride, indium nitride, an indium nitride gallium mix crystal, a gallium-aluminum-nitride mix crystal, or an indium nitride aluminum gallium mix crystal is mentioned.

[0031]This micro crystallite may contain a n type impurity if needed. Since it incidentally has a career based on an oxygen deficiency in many cases when an oxide constitutes micro crystallite, it becomes an n-type semiconductor which has electron transport property in many cases.

[0032]The particle sintered compact 10 which has such composition can be manufactured as follows.

[0033]First, the particles 11 containing the micro crystallite which consists of a semiconductor mentioned above are distributed in a solution, and a coating solution is produced. As for the crystal grain diameter of micro crystallite, it is preferred that they are 100 nm or less and also 50 nm or less as mentioned above.

[0034]The organic solvent which contains at least one sort of organic compounds which have one or more hydroxyl groups as a solution which distributes the particles 11, for example is preferred. The univalent alcohol specifically represented by ethanol, methanol, n-propyl alcohol, i-propyl alcohol,

1-butanol, or 2-butanol, Or the divalent alcohol represented by ethylene glycol, a diethylene glycol, 2-methoxyethanol, 2-ethoxyethanol, or triethylene glycol and its derivative, Or aromatic compounds, such as polyhydric alcohol more than trivalent [ which is represented by glycerin ], phenol, or cresol, may be mentioned, these two or more sorts may be mixed and used, and these at least one sort and other organic compounds may be mixed and used.

[0035]Although the quantity of the solution which distributes the particles 11 can be set up arbitrarily, since coating film thickness in case this applies a coating solution is controlled, it is necessary to mind. Idiomatic dispersion means, such as stirring, a ball mill, a sand mill, and ultrasonic dispersion, may be sufficient as the dispersion method of the particles 11, and a uniform coating solution is easily obtained by these dispersion means.

[0036]Subsequently, this coating solution is applied on the proper substrate which is not illustrated, stoving, such as natural seasoning or oven, is performed, and a coating layer is formed. To a substrate, in that case, for example, A glass substrate, a ceramics board, silicon on sapphire, a boron nitride (BN) board, an aluminum nitride substrate, a gallium nitride substrate, a gallium-aluminum-nitride board, an indium nitride gallium board, a silicon carbide (SiC) board, a silicon (Si) board, or a metal substrate, Or the resin substrate which consists of polycarbonate resin, polyethylene terephthalate resin, polyester resin, an epoxy resin, an acrylic resin, or ABS (Acrylonitrile-Butadiene-Styrene copolymer) resin. It can use.

[0037]The coating method of a coating solution may be arbitrary and can apply variously a spin coat method, a dip coating method, a spray coating method, the roll coat method, the meniscus coat method, the bar coat method, the curtain flow coat method, the bead coat method, etc. This spreading and desiccation are repeatedly performed until a coating layer serves as predetermined thickness.

[0038]Then, this coating layer is sintered with heating. By this, solid phase sintering between the particles in a coating layer is promoted, and the grain boundary energy barrier between particles is eased, and a mechanical strength increases by eburation. That is, the particle sintered compact 10 shown in drawing 1 is obtained. It may be made to heat using firing furnaces, such as an electric firing furnace, and may be made to heat by irradiating with energy beams, such as a laser beam, for example in that case.

[0039]For example, when sintering the particles 11 containing the micro crystallite which consists of oxides, such as a zinc oxide, using a firing furnace, it is preferred more than 60mol% and that the content ratio of oxygen (O<sub>2</sub>) heats at the temperature of about 600 °C in the gas atmosphere beyond 90mol% preferably. It is because oxygen will be desorbed from the surface of micro crystallite at the time of heating and an oxygen deficiency will increase the content ratio of oxygen, if more than 60mol% and using more than 90mol% more preferably have a low oxygen content ratio. In sintering the particles 11 containing the micro crystallite which consists of nitrides, it introduces nitrogen (N<sub>2</sub>) into a gas atmosphere instead of oxygen.

[0040]In sintering the particles 11 containing the micro crystallite which irradiates with a laser beam and consists of oxides, for example, it is preferred more than 60mol% and that the content ratio of oxygen irradiates with an excimer laser beam with the energy density about 150 mJ/cm<sup>2</sup> into the gas atmosphere beyond 90mol% preferably. What is necessary is for it to be the same as that of the case where a firing furnace is used to carry out the content ratio of oxygen in this way, and just to introduce nitrogen instead of oxygen, in calcinating the particles 11 containing the micro crystallite which consists of nitrides. As an excimer laser beam, for example XeCl (wavelength of 308 nm), What has the wavelength of the ultraviolet region oscillated using XeF (wavelength of 351 nm), XeBr (wavelength of 282 nm), KrF (wavelength of 248 nm), KrCl (wavelength of 222 nm) or ArF (wavelength of 193 nm), F<sub>2</sub> (wavelength of 157 nm), etc. can be used.

[0041]This particle sintered compact 10 acts as follows.

[0042]In this particle sintered compact 10, if current is poured in, luminescence will take place by the electronic-electron hole recombination resulting from forbidden-band transition or transition between donor acceptor level. Here, since the particles 11 are joined by the sintering region 11a, the carrier transport nature between particles is secured and good luminescence is obtained by the low voltage.

[0043]Thus, since according to this particle sintered compact 10 the particles 11 are sintered and the particles 11 were joined by the sintering region 11a, the grain boundary energy barrier between particles can be made small, and the carrier transport nature between particles can be secured. Therefore, good luminescence can be easily obtained by the low voltage. Since it is joined by the sintering region 11a, a high mechanical strength can also be obtained.

[0044]Such a particle sintered compact 10 is used for the light emitting device which starts this embodiment as follows.

[0045](The 1st light emitting device) Drawing 3 expresses the outline composition of the light emitting diode (light emitting diode; LED) which is the 1st light emitting device concerning this embodiment. (A) is the planar structure seen from the electrode side, and (B) is the section structure which met the I-I line of (A). This light emitting diode has the structure which the hole transporting bed 22 which is the 1st conductivity type layer, and the semiconductor light layer 23 which consists of the particle sintered compact 10 mentioned above adjoined on the substrate 21, and was laminated by this order. The various base explained in the manufacturing method of the particle sintered compact 10 can be used for the substrate 21, for example.

[0046]The thickness (only henceforth thickness) of a laminating direction is about 0.1 micrometer - 10 micrometers, and the hole transporting bed 22 is constituted by the nitride of 3B group element which added p type impurities, such as magnesium (Mg), for example. The carrier concentration of the hole transporting bed 22 is a  $1.0 \times 10^{16} \text{cm}^{-3}$  -  $1.0 \times 10^{20} \text{cm}^{-3}$  grade, for example. The hole transporting bed 22 may have what kind of gestalten, such as a single crystal body, the polycrystalline substance, amorphous bodies, particle objects, or these complexes.

[0047]As for the hole transporting bed 22, it is preferred to have bigger forbidden-band width energy than the semiconductor light layer 23. Thereby, it is because the hole transporting bed 22 can be operated as eye career \*\*\*\*\* to the semiconductor light layer 23, and a cladding layer. Since the light emitted from the semiconductor light layer 23 rather than the absorption edge wavelength of the hole transporting bed 22 by the direction of the wavelength of the light emitted from the semiconductor light layer 23 becoming long is penetrated without decreasing the inside of the hole transporting bed 22, it is because light can be taken out from the substrate 21 side and optical extraction efficiency can be increased.

[0048]For example, when it constitutes so that it may mention later, and the semiconductor light layer 23 may contain the micro crystallite which consists of a zinc oxide, titanium oxide, or iron oxide, it is preferred to constitute the hole transporting bed 22 with boron nitride, aluminum nitride, gallium nitride, a gallium-aluminum-nitride mix crystal, etc. Incidentally a zinc oxide those forbidden-band width energies 3.2 eV, In titanium oxide, 6.2 eV and aluminum nitride are 6.1 eV, gallium nitride is 3.4 eV, and, in the case of a mix crystal, 3.1 eV and boron nitride change [ 3.0 eV and iron oxide ( $\text{Fe}_2\text{O}_3$ ) ] according to the presentation.

[0049]Thickness is about 0.5 micrometer - 10 micrometers, and the semiconductor light layer 23 is constituted by the particle sintered compact 10 containing the micro crystallite which consists of oxides, for example. As this oxide, as mentioned above, the thing containing at least one sort in the group which consists of zinc, titanium, and iron is mentioned, for example. This particle sintered compact 10 has a career by an oxygen deficiency, and, thereby,

this semiconductor light layer 23 is an electron transport layer which is the 2nd conductivity type layer.

[0050] On the hole transporting bed 22, the p lateral electrode 24 which is the 1st electrode is formed, and the n lateral electrode 25 which is the 2nd electrode is formed on the semiconductor light layer 23. The p lateral electrode 24 is electrically connected with the semiconductor light layer 23 via the hole transporting bed 22 and the hole transporting bed 22, respectively, for example, it has the structure which laminated a nickel (nickel) layer, a platinum (Pt) layer, and the golden (Au) layer one by one, and alloyed them from the hole transporting bed 22 side. The n lateral electrode 25 is electrically connected with the semiconductor light layer 23, for example, it has the structure which vapor-deposited and alloyed the gold layer. As for the n lateral electrode 25, it is preferred to be formed almost to the whole surface of the semiconductor light layer 23. It is because the touch area of the semiconductor light layer 23 and the n lateral electrode 25 becomes large and luminescence can be obtained almost from the whole surface of the semiconductor light layer 23.

[0051] The light emitting diode which has such composition can be manufactured as follows.

[0052] First, on the washed substrate 21 for example, the MOCVD method, an MBE technique, and PLD (Pulsed Laser Deposition; pulse laser membrane formation) -- the hole transporting bed 22 is formed using law, sputtering process, or the CVD (Chemical Vapor Deposition) method.

[0053] Subsequently, it forms on the hole transporting bed 22 by the method which mentioned the semiconductor light layer 23 above. Then, form the resist pattern which stripe shape does not illustrate, for example corresponding to the formation position of the p lateral electrode 24 on the semiconductor light layer 23, and this resist pattern is used as a mask. For example, the semiconductor light layer 23 is selectively removed by a reactive-ion-etching (RIE; Reactive Ion Etching) method, and the hole transporting bed 22 is exposed.

[0054] The resist pattern which is not illustrated is removed, after exposing the hole transporting bed 22, on the semiconductor light layer 23, vapor-deposit a gold layer and the n lateral electrode 25 is formed, and on the exposed hole transporting bed 22, sequent deposition of a nickel layer, a platinum layer, and the gold layer is carried out, and the p lateral electrode 24 is formed. After it, heat-treatment is performed and the p lateral electrode 24 and the n lateral electrode 25 are alloyed. Thereby, the light emitting diode shown in drawing 3 (A) and (B) is obtained.

[0055] Thus, the light emitting diode manufactured acts as follows.

[0056] This light emitting diode operates according to a direct current, when predetermined voltage is impressed between the p lateral electrode 24 and the n lateral electrode 25, current is injected into the semiconductor light layer 23, and [ near the interface of the semiconductor light layer 23 and the hole transporting bed 22 ], luminescence takes place by electronic-electron hole recombination. Here, since the oxide constitutes the micro crystallite contained in the semiconductor light layer 23, ultraviolet radiation or visible light is emitted. Since the particle sintered compact 10 constitutes the semiconductor light layer 23, the carrier transport nature in the semiconductor light layer 23 is secured, and good luminescence is obtained by the low voltage.

[0057] This light emitting diode is used as light sources, such as lighting, a display, or germicidal lamp glass.

[0058] Thus, since it had the semiconductor light layer 23 which consists of the particle sintered compact 10 according to this light emitting diode, the carrier transport nature in the semiconductor light layer 23 can be secured, and it can be made to operate easily by a direct current of the low voltage. Therefore, a complicated and expensive drive circuit is not needed but it can be used as a display device of the electric product used on the outdoors, such as a cellular phone.

[0059] It can form on the arbitrary substrates 21 and it is not necessary to use

the substrate which was excellent in heat resistance compared with the case where it forms with epitaxial grown methods, such as the MOCVD method. Therefore, the construction material of the substrate 21 can be chosen arbitrarily, and area of the substrate 21 can be enlarged, and a manufacturing cost can be reduced. Therefore, it becomes possible to realize large-sized display devices, such as a large area display and a large area light.

[0060]When forming the semiconductor light layer 23, it is not necessary to control a crystal system and a grating constant precisely, and they can be manufactured easily.

[0061]In addition, since oxides, such as a zinc oxide, constituted micro crystallite according to this light emitting diode, in a room temperature, ultraviolet luminescence can be carried out easily. Therefore, it is applicable to a display, a light, etc. by using as the fluorescent substance excitation light source. For example, by using in the image display element based on coloring of a fluorescent substance as a source of excitation energy replaced with the electron gun of CRT (CathodeRay Tube), or the cold cathode of FED (FieldEmission Display), A large-sized planar display is realizable.

[0062](The 2nd light emitting device) Drawing 4 expresses notionally the composition of the light emitting diode which is the 2nd light emitting device concerning this embodiment. (A) is the planar structure seen from the electrode side, and (B) is the section structure which met the II-II line of (A). The electron transport layer 36 which is the 2nd conductivity type layer is formed between the semiconductor light layer 23 and the n lateral electrode 25, and this light emitting diode has the same composition as the 1st light emitting device except for the n lateral electrode 25 electrically having been connected with the semiconductor light layer 23 via the electron transport layer 36. Therefore, the same numerals are given to the same component here, and the detailed explanation is omitted.

[0063]Thickness is about 0.5 micrometer - 10 micrometers, and the electron transport layer 36 is constituted by the nitride of 3B group element which added n type impurities, such as silicon (Si), for example. The carrier concentration of the electron transport layer 36 is a  $1.0 \times 10^{17} \text{cm}^{-3}$  -  $1.0 \times 10^{20} \text{cm}^{-3}$  grade, for example. As for this electron transport layer 36, it is preferred to have what kind of gestalten, such as a single crystal body, the polycrystalline substance, amorphous bodies, particle objects, or these complexes, and to have bigger forbidden-band width energy than the semiconductor light layer 23 like the hole transporting bed 22.

[0064]Although the semiconductor light layer 23 had turned into an electron transport layer in the 1st light emitting device, it does not need to be an electron transport layer in this light emitting device. The n lateral electrode 25 does not necessarily need to be formed all over the electron transport layer 36.

[0065]This light emitting device can be manufactured like the 1st light emitting device. The electron transport layer 36 can be formed like the hole transporting bed 22. This light emitting device acts like the 1st light emitting device except for the thing of the semiconductor light layer 23 which luminescence takes place in the whole mostly. This light emitting device is used like the 1st light emitting device, and can acquire the same effect.

[0066]

[Example]The concrete example of this invention is described in detail with reference to drawings. The following examples attach and explain the same numerals with reference to drawing 3 used in the above-mentioned embodiment.

[0067](Example 1) After it prepared for the surface of 20 mm long, the side of 20 mm, and 1 mm in height a size first the substrate 21 which consists of sapphire to which the crystalline-lattice c side was exposed and neutral detergent washed, it rinsed and cleaned ultrasonically using the organic solvent further.

[0068]Subsequently, conveying the washed substrate 21 in an MOCVD system, and supplying hydrogen gas ( $\text{H}_2$ ) in a device by the flow of  $2 \text{dm}^3/\text{min}$  in ordinary

pressure, gas phase etching of the substrate 21 was carried out with the substrate temperature of 1050 \*\*, and the surface roughness of the substrate was made to increase.

[0069]Then, holding substrate temperature, after the temperature of the substrate 21 shall be 1000 \*\*, 20dm<sup>3</sup>/min, and ammonia gas (NH<sub>3</sub>) for hydrogen gas 10dm<sup>3</sup>/min, The dimethyl magnesium gas diluted by 2.2 ppm with 1.8x10<sup>-4</sup>mol/min and hydrogen gas in trimethylgallium is supplied for 30 minutes in a device with the speed of 200-cm<sup>3</sup>/min, respectively, On the substrate 21, the hole transporting bed 22 which consists of single crystal p type gallium nitride of 5.0-micrometer [ in thickness ] and carrier concentration 7.8x10<sup>19</sup>cm<sup>-3</sup> was formed.

[0070]Ultrasonic dispersion of the micro crystallite powder (C.I. Kasei make; mean particle diameter of 31 nm) of the zinc oxide produced by the gaseous phase method was carried out by the concentration of 10 mass % into ethanol, and the coating solution was produced. After it, this coating solution was applied at the number of rotations of 1000 rpm by the spin coating method on the hole transporting bed 22, and natural seasoning was carried out. After repeating this application process 5 times in total and forming a coating layer, the electric firing furnace was used, into the oxygen gas atmosphere of 100% of concentration, it heated at the temperature of 600 \*\* for 1 hour, and the semiconductor light layer 23 with a thickness of 2.5 micrometers which sinters a coating layer and consists of zinc oxides was formed.

[0071]After forming the semiconductor light layer 23, corresponding to the formation position of the p lateral electrode 24, the resist pattern of stripe shape was formed on this semiconductor light layer 23. The positive resist for i line exposure by TOKYO OHKA KOGYO CO., LTD. was used for resist. The semiconductor light layer 23 was selectively removed by the reactive-ion-etching method by having used this resist pattern as the mask after it, and a part of hole transporting bed 22 was exposed.

[0072]After exposing a part of hole transporting bed 22, the resist pattern was removed, on almost the whole surface of the semiconductor light layer 23, electron beam vacuum evaporation of the 500-nm-thick gold layer was carried out, and the n lateral electrode 25 was formed. On the exposed hole transporting bed 22, electron beam vacuum evaporation of a 10-nm-thick nickel layer, a 100-nm-thick platinum layer, and the 500-nm-thick gold layer was carried out at order, and the p lateral electrode 24 was formed. Into the nitrogen gas atmosphere of 100% of concentration, heat-treatment was performed for 20 minutes at the temperature of 600 \*\* after it, and the p lateral electrode 24 and the n lateral electrode 25 were alloyed. This produced the light emitting device as shown in drawing 3.

[0073]Thus, about the obtained light emitting device, luminescent characteristic evaluation by room temperature photoluminescence (PL;Photoluminescence) measurement of the hole transporting bed 22 and the semiconductor light layer 23 was performed. In room temperature photoluminescence measurement, strong excitation was carried out using helium-Cd laser (the wavelength of 325 nm, output of 25 mW) as the excitation light source, and spectrum analysis was conducted with the spectrophotometer (the product made by Jobin-Yvon, HR-320). PL emission spectrum obtained by drawing 5 is shown. In drawing 5, a vertical axis expresses luminescence intensity, and the horizontal axis expresses wavelength (unit; nm).

[0074]About the semiconductor light layer 23, the peak of PL luminescence intensity with a wavelength of 380 nm considered to be direct transition luminescence was accepted so that drawing 5 might show. That is, it was checked that this semiconductor light layer 23 has the luminescent material characteristic. The peak of PL luminescence intensity considered to be based on an oxygen deficiency in the range with a wavelength of 500 nm - 600 nm was also observed in the semiconductor light layer 23. On the other hand, it turned out that the peak of PL luminescence intensity is not accepted about the hole

transporting bed 22, and it does not have the luminescent material characteristic.

[0075]After forming a coating layer via the hole transporting bed 22 as a comparative example over this example on the substrate 21, before sintering, luminescent characteristic evaluation was performed like the semiconductor light layer 23 of this example about this coating layer. PL emission spectrum of the obtained coating layer is shown in drawing 6 with PL emission spectrum of the semiconductor light layer 23. The vertical axis and horizontal axis of drawing 6 are the same as that of drawing 5.

[0076]The peak with a wavelength of 500 nm - 600 nm considered to be based on the peak with a wavelength of 380 nm and oxygen deficiency which are considered to be direct transition luminescence about a coating layer as well as the semiconductor light layer 23 was accepted, respectively so that drawing 6 might show. However, the coating layer of PL luminescence intensity with a wavelength of 380 nm considered to be direct transition luminescence was stronger than the semiconductor light layer 23, and the coating layer of PL luminescence intensity with a wavelength of 500 nm - 600 nm considered to be based on an oxygen deficiency was weaker than the semiconductor light layer 23. That is, the coating layer had few oxygen deficiencies and it turned out that the oxygen deficiency of the semiconductor light layer 23 has increased. Therefore, the semiconductor light layer 23 is imagined to be that in which an oxygen deficiency increases by sintering and electron transport property increases by that cause.

[0077]About the semiconductor light layer 23, the sample of monolayer structure was produced on the substrate which consists of sapphire apart from a light emitting device, and electrical property evaluation was performed with a hole (Hall) evaluation-of-effectiveness device (Nippon Bio-Rad Laboratories HL-5500C). As a result, it turned out that specific resistance is  $8.2 \times 10^3 \Omega \text{cm}$  and this semiconductor light layer 23 has electron transport property. When electrical property evaluation was performed also about the coating layer before sintering this sample with the four-poles four point probe method resistivity meter (Mitsubishi Chemical Loresta-GP), specific resistance is more than  $1 \times 10^7 \Omega \text{cm}$  of a limit-of-measurement value, and it turned out that it does not have electron transport property. That is, it turned out that electron transport property ( $0.001 \Omega \text{cm}$  of specific resistance cm -  $10000 \Omega \text{cm}$  grade) reveals the semiconductor light layer 23 by sintering.

[0078]In addition, the crystallized state was observed about the semiconductor light layer 23 by X-ray diffraction measurement (XRD; X-ray Diffraction) and section TEM (Transmission Electron Microscope). As a result, this semiconductor light layer 23 has the structure where micro crystallite was joined by sintering.

It turned out that the crystal grain diameter is about an average of 40 nm from a TEM photograph.

[0079]Current/voltage characteristics (I-V characteristic) were evaluated about the obtained light emitting device again. The result is shown in drawing 7. In drawing 7, a vertical axis expresses current (unit; mA), and the horizontal axis expresses impressed electromotive force (unit; V). the case where it impresses so that the polarity (+ in a figure and numerals of -) of impressed electromotive force may become the p lateral electrode 24 of a light emitting device with positive potential and may become the n lateral electrode 25 with negative potential -- right (+sign) -- it carried out.

[0080]In this light emitting device, the diode characteristics of good rectification were accepted so that drawing 7 might show. That is, as for this light emitting device, it was checked that pn junction is formed of the hole transporting bed 22 and the semiconductor light layer 23.

[0081]In addition, simultaneously with above-mentioned current/voltage-characteristics evaluation, luminescent characteristic



evaluation by room temperature EL (Electroluminescence) measurement was performed again. In room temperature EL measurement, a collimator lens 5 mm in diameter is stuck at the rear face (near field in which the semiconductor light layer 23 is not formed) of the substrate 21 of a light emitting device. An optical fiber cable 1 mm in inside diameter was connected to this collimator lens, and spectrum analysis was conducted with the spectrophotometer (Ocean Optics, Inc. company make S2000). The EL luminescence spectrum acquired by drawing 8 is shown. In drawing 8, a vertical axis expresses luminescence intensity, and the horizontal axis expresses wavelength (unit; nm). Impressed electromotive force at the time of EL measurement was set to 10V with forward voltage (polarity; +sign).

[0082]In this light emitting device, the peak of EL luminescence with a wavelength of 400 nm considered to originate in the direct transition of the zinc oxide micro crystallite in the semiconductor light layer 23 was accepted so that drawing 8 might show. That is, this light emitting device operated according to a direct current, and having a luminescent characteristic which emits the ultraviolet radiation which originates in direct transition in a room temperature was checked.

[0083](Example 2) After it first prepared the substrate 21 which consists of synthetic quartz of 20 mm long, the side of 20 mm, and 1 mm in height a size and neutral detergent washed, it rinsed and cleaned ultrasonically using the organic solvent further.

[0084]Subsequently, the hole transporting bed 22 which uses a PLD device and consists of polycrystal p type aluminum nitride of 1.1-micrometer [ in thickness ] and carrier concentration  $3.5 \times 10^{16} \text{cm}^{-3}$  was formed on this substrate 21. The ArF excimer laser film deposition system by Lambda Physik A.G. (laser wavelength; 193 nm) was used for the PLD device.

[0085]Drawing 9 expresses the outline composition of the PLD device. This PLD device is provided with the vacuum chamber 43 which consists of stainless steel to which the gas supply line 41 and the gas exhaust pipes 42 were connected, respectively. Inside the vacuum chamber 43, the substrate holder 44 which lays the substrate 21, and the target adapter plate 46 furnished with the target 45 are allocated, respectively so that it may counter mutually. Although drawing 9 shows the case where the one target adapter plate 46 is allocated, two or more target adapter plates 46 may be allocated. The target 45 can be irradiated now with the pulse laser L through the laser incident port 47 with the pulsed laser apparatus which was allocated in the exterior of the vacuum chamber 43 and which is not illustrated. The heating method which a heater etc. do not illustrate is provided in the inside of the vacuum chamber 43. Thereby, the substrate 21 can be heated now.

[0086]Here, the following operations were specifically performed using such a PLD device. First, the washed substrate 21 was laid in the substrate holder 44, and the target 45 which consists of an aluminum Magnesium alloy (AlMg alloy) was attached to the target adapter plate 46. The presentation by Sumitomo Metal Mining Co., Ltd. used aluminum 99 mass % magnesium 1 mass %, and purity used the thing more than 99.9 mass % for the target 45.

[0087]Subsequently, the gas in the vacuum chamber 43 was exhausted from the gas exhaust pipes 42, and the inside of the vacuum chamber 43 was made into the decompressed atmosphere about  $2.7 \times 10^{-5} \text{Pa}$ . Then, having heated the substrate 21 at 500 °C with the heater which is not illustrated, and holding substrate temperature, it supplied until it reached the nitrogen gas of 100% of concentration in the vacuum chamber 43 via the gas supply line 41 at the pressure of about 6.7 Pa. The target 45 was irradiated with the pulse laser with the energy density of 200 mJ/cm<sup>2</sup> after it, and the hole transporting bed 22 was formed by the reactant laser abrasion D.

[0088]Thus, after forming the hole transporting bed 22, the semiconductor light layer 23 with a thickness of 2.4 micrometers which consists of zinc oxides was

formed like the 1st example. Like the 1st example after it, the p lateral electrode 24 and the n lateral electrode 25 were formed, respectively, and the alloying by heating was performed and the light emitting device as shown in drawing 3 was produced. However, in formation of the p lateral electrode 24, the thickness of the nickel layer was 50 nm. Heat treating time of alloying was carried out for 60 minutes.

[0089]When luminescent characteristic evaluation of the hole transporting bed 22 and the semiconductor light layer 23, observation of the crystallized state of the semiconductor light layer 23, current/voltage-characteristics evaluation of an element, and luminescent characteristic evaluation of the element were performed like Example 1 about the obtained light emitting device, respectively, the result as Example 1 with same all was obtained. That is, even if the single crystal constituted the hole transporting bed 22 and polycrystal constituted, it was checked that the high characteristic can be obtained regardless of the gestalt.

[0090](Example 3) replacing with an electric firing furnace, when forming the semiconductor light layer 23 -- an ArF excimer laser device (the Lambda Physik A.G. make.) Laser wavelength; except for having heated and sintered the coating layer, others produced the light emitting device like Example 1 using 193 nm by irradiating with laser with the energy density of 60 mJ/cm<sup>2</sup>.

[0091]About the obtained light emitting device, like Example 1, luminescent characteristic evaluation of the hole transporting bed 22 and the semiconductor light layer 23, When electrical property evaluation of the semiconductor light layer 23, observation of the crystallized state of the semiconductor light layer 23, current/voltage-characteristics evaluation of an element, and luminescent characteristic evaluation of the element were performed, respectively, the result as Example 1 with same all was obtained. That is, it was checked that the same semiconductor light layer 23 as the case where it heats with an electric firing furnace can be obtained also by laser annealing.

[0092](Examples 4 and 5) Replace with the micro crystallite powder of a zinc oxide, and the micro crystallite powder (C.I. Kasei make; mean particle diameter of 30 nm) of titanium oxide is used in Example 4, In Example 5, others produced the light emitting device like Example 1 except for having formed the semiconductor light layer 23 using the micro crystallite powder (C.I. Kasei make; mean particle diameter of 21 nm) of iron oxide (Fe<sub>2</sub>O<sub>3</sub>), respectively.

[0093]It is made to be the same as that of Example 1 about the light emitting device of acquired Examples 4 and 5, When luminescent characteristic evaluation of the hole transporting bed 22 and the semiconductor light layer 23, electrical property evaluation of the semiconductor light layer 23, observation of the crystallized state of the semiconductor light layer 23, current/voltage-characteristics evaluation of an element, and luminescent characteristic evaluation of the element were performed, respectively, the result as Example 1 with same all was obtained. About the semiconductor light layer 23 of Examples 4 and 5, the peak of PL luminescence intensity was accepted in the visible light wavelength, respectively. Example 4 of the specific resistance of these semiconductor light layer 23 is  $9.1 \times 10^3 \Omega \text{cm}$ .

Example 5 was  $9.8 \times 10^3 \Omega \text{cm}$ .

Incidentally, both the specific resistance of the coating layer before sintering them was more than  $1 \times 10^7 \Omega \text{cm}$  of a limit-of-measurement value. That is, it was checked that the semiconductor light layer 23 can be constituted with other oxides.

[0094]As mentioned above, although the embodiment and the example were given and this invention was explained, this invention is not limited to the above-mentioned embodiment and an example, and is variously deformable. For example, although the case where an oxide or a nitride constituted the micro crystallite in the particle sintered compact 10 was explained, other semiconductor materials can also constitute from the above-mentioned embodiment. For example, at least one sort of two group elements chosen from

the group which consists of zinc, magnesium (Mg), cadmium (Cd), manganese (Mn), mercury (Hg), and beryllium (Be). Other II-VI group compound semiconductors containing at least one sort of six group elements chosen from the group which consists of oxygen (O), selenium (Se), sulfur (S), and a tellurium (Te). Or at least one sort of three group elements chosen from the group which consists of boron, aluminum, gallium, and indium. Other groups III-V semiconductor containing at least one sort of five group elements chosen from the group which consists of nitrogen (N) Lynn (P), arsenic (As), antimony (Sb), and bismuth (Bi) can also constitute.

[0095]Although the case where the particle sintered compact 10 containing the micro crystallite which consists of oxides constituted the semiconductor light layer 23 from the above-mentioned embodiment and the above-mentioned example was explained, it may be made for the particle sintered compact containing the micro crystallite which consists of nitrides to constitute, and may be made for the particle sintered compact containing the micro crystallite which consists of other semiconductor materials mentioned above to constitute.

[0096]Although the concrete example was given and explained about the material which constitutes the hole transporting bed 22 and the electron transport layer 36, respectively, it may be made for other materials to constitute them from the above-mentioned embodiment. As a material which constitutes the hole transporting bed 22 and the electron transport layer 36, not only an inorganic material but organic materials can also be used.

[0097]In addition, by the above-mentioned embodiment, when the hole transporting bed 22 and the semiconductor light layer 23 were laminated one by one to the substrate 21, explained the case where the hole transporting bed 22, the semiconductor light layer 23, and the electron transport layer 36 were laminated one by one to the substrate 21, but. It may be made to laminate a semiconductor light layer and a hole transporting bed one by one to a substrate, and may be made to laminate an electron transport layer, a semiconductor light layer, and a hole transporting bed one by one to a substrate.

[0098]Although the 1st conductivity type layer was made into the hole transporting bed and the 2nd conductivity type layer was used as the electron transport layer by the above-mentioned embodiment again, the 1st conductivity type layer is used as an electron transport layer, and it is good also considering the 2nd conductivity type layer as a hole transporting bed.

[0099]In addition, although the above-mentioned embodiment mentioned and explained the light emitting diode concrete as an example of a light emitting device again, this invention is widely applicable also to the light emitting diode which has other composition. For example, it is good also as a laminated structure which consists a hole transporting bed or an electron transport layer of two or more layers. For example, it may be made to provide the 1st electrode and 2nd electrode in the semiconductor light layer which consists of the particle sintered compact 10. This invention is applicable to other light emitting devices, such as a laser diode, again. That is, this invention is widely applicable to the light emitting device provided with the semiconductor light layer which consists of the particle sintered compact 10.

[0100]

[Effect of the Invention]Since the particles containing the micro crystallite of a semiconductor were provided with the semiconductor light layer which consists of a particle sintered compact joined by the sintering region according to the light emitting device according to any one of claims 1 to 24 as explained above, Since the semiconductor light layer was formed with the particle sintered compact which sintered the particles containing the micro crystallite of a semiconductor according to the manufacturing method of the light emitting device according to any one of claims 25 to 49, The carrier transport nature in a semiconductor light layer can be secured, and it can be made to operate easily by a direct current of the low voltage. Therefore, a complicated and expensive drive circuit is not needed but the effect that it can be used as a display device

of the electric product used on the outdoors, such as a cellular phone, is done so.

[0101]It can form on arbitrary substrates and it is not necessary to use the substrate which was excellent in heat resistance compared with the case where it forms with epitaxial grown methods, such as the MOCVD method. Therefore, the construction material of a substrate can be chosen arbitrarily, and area of a substrate can be enlarged, and the effect that a manufacturing cost can be reduced also does so. It is not necessary to control a crystal system and a grating constant precisely in formation of a semiconductor light layer, and the effect that it can manufacture easily also does so.

[0102]Since the zinc oxide constituted micro crystallite especially according to the light emitting device given in any 1 of claim 5, claim 17, claim 27, or claims 39, in a room temperature, ultraviolet luminescence can be carried out easily. Therefore, the effect that it is applicable to a display, a light, etc. is done so by using as the fluorescent substance excitation light source. For example, in the image display element based on coloring of a fluorescent substance, a large-sized planar display is realizable by using as a source of excitation energy replaced with the electron gun of CRT, or the cold cathode of FED.

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1]It is a key map showing the composition of the particle sintered compact used for the light emitting device concerning an embodiment of the invention.

[Drawing 2]It is a key map showing the particulate aggregate before sintering.

[Drawing 3](A) is a top view showing the example of 1 composition of the 1st light emitting device concerning an embodiment of the invention, and (B) is the sectional view which met the I-I line of (A).

[Drawing 4](A) is a top view showing the example of 1 composition of the 2nd light emitting device concerning an embodiment of the invention, and (B) is the sectional view which met the II-II line of (A).

[Drawing 5]It is PL emission spectrum of a semiconductor light layer and a hole transporting bed concerning Example 1 of this invention.

[Drawing 6]It is PL emission spectrum of the coating layer concerning the semiconductor light layer and comparative example concerning Example 1 of this invention.

[Drawing 7]It is a characteristic figure showing the current/voltage characteristics (I-V characteristic) of the light emitting device concerning Example 1 of this invention.

[Drawing 8]It is an EL luminescence spectrum of the light emitting device concerning Example 1 of this invention.

[Drawing 9]It is a sectional view showing the outline composition of the pulse laser film deposition system used when forming a hole transporting bed in Example 2 of this invention.

### [Description of Notations]

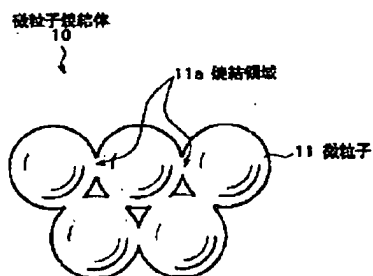
10 [ -- Substrate, ] -- A particle sintered compact, 11 -- Particles, 11a -- A sintering region, 21 22 -- A hole transporting bed (the 1st conductivity type layer), 23 -- A semiconductor light layer, 24 -- p lateral electrode (the 1st electrode), 25 -- n lateral electrode (the 2nd electrode), 36 -- Electron transport layer (the 2nd conductivity type layer), 41 [ -- A substrate holder, 45 / -- A target, 46 / -- A target adapter plate, 47 / -- A laser incident port, L / -- A pulse laser, D / -- Ablation. ] -- A gas supply line, 42 -- Gas exhaust pipes, 43 -- A vacuum chamber, 44

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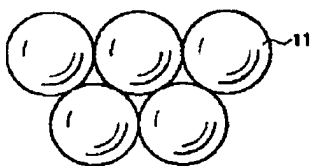
## DRAWINGS

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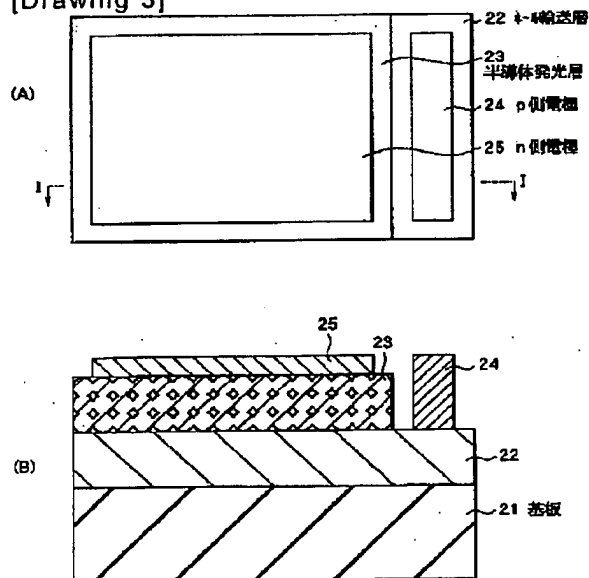
[Drawing 1]



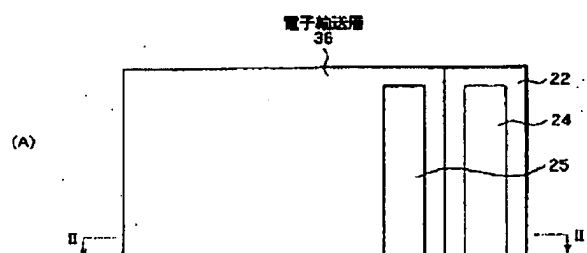
[Drawing 2]



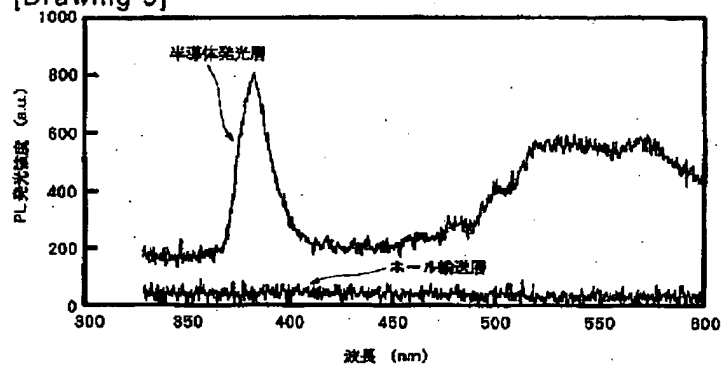
[Drawing 3]



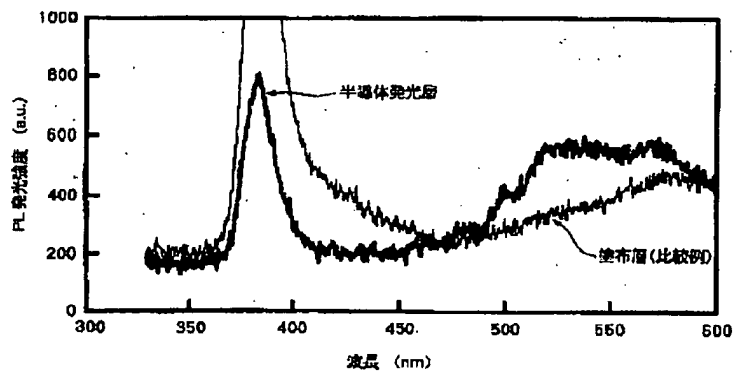
[Drawing 4]



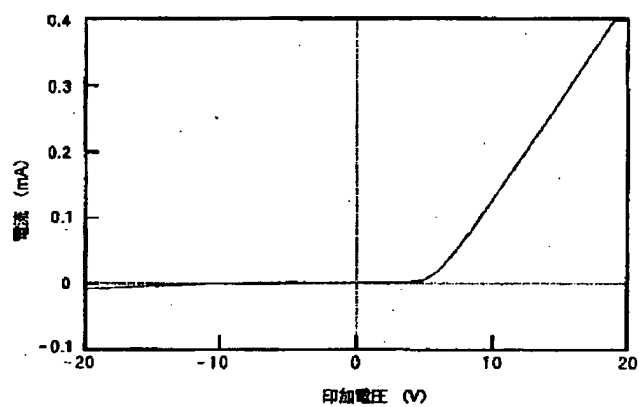
[Drawing 5]



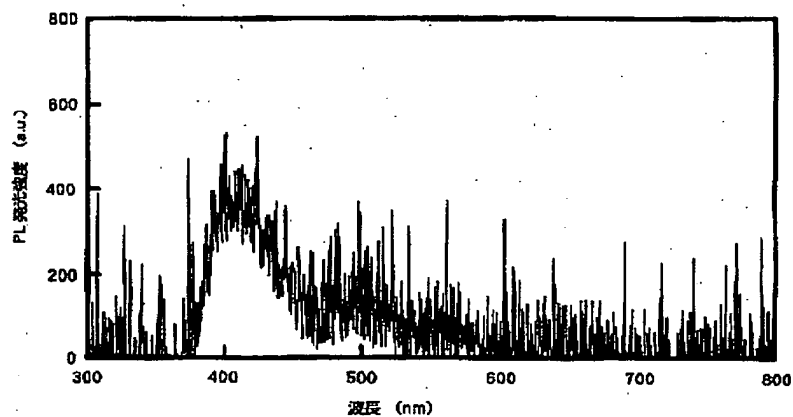
[Drawing 6]



[Drawing 7]



[Drawing 8]



[Drawing 9]

